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VISCOSITY DEPENDENCE OF THE ROTATIONATIONAL REORIENTATION OF COUMARINS BY DEPOLARIZATION TECHNIQUE

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Abstract:

Steady-state and time-resolved fluorescence behavior of coumarin 6 (C6) and coumarin 7 (C7) in alkane and alcohol solvents has been investigated. Steady-state absorption and emission spectral behavior of C6 and C7 is found not to be affected by the both the solvents. Time-resolved fluorescence anisotropy measurements show that the rotational reorientation of the probe becomes faster in alcohol. A comparison of the experimentally measured rotational reorientation times of C6 and C7 are identical in a given solvents at a particular temperature. The present study has been undertaken to examine the role of friction experienced by the polar solutes in a polar and non-polar solvents. Molecular shape and size are similar but the friction experienced by these probes in n-tridecane and n-propanol solvents viscosities were varies by temperature. However, it was observed that C6 and C7 rotates faster in alcohol than alkane and the observed results are discussed in the last section.

Key Words: Coumarin laser dyes, anisotropy, lifetime, rotational reorientation times.

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Introduction:

The 1,2-benzopyron derivatives, known as the coumarin dyes, in recent years coumarins are more important in the field of physical chemistry, owing to their interesting photophysical and photochemical properties. Among the coumarin dyes, the 7-aminocoumarins compose a special class of compounds. Experimental results observed

that the Stokes shifts, fluorescence quantum yields and fluorescence lifetimes of 7-aminocoumarins in nonpolar solvents are often significantly different from those in polar solvents [1-14]. The explanation for such unusual behavior of 7-aminocoumarins in the solvent polarity [1-10], and hydrogen bonding etc., [11-14], such unusual behavior of 7-aminocoumarins in the solvent polarity and hydrogen bonding etc., were observed [15-17]. Three types of hydrogen bond [12-14] can be formed for the 7-aminocoumarins, which include participation of the amino nitrogen lone pair (type i), carbonyl oxygen (type ii), and amino hydrogen (type iii) with hydrogen-bonding solvents. The type (i) is more probable in the ground state, whereas the types (ii) and (iii) are more important in the first excited state [12] assumed by Arbeloa et al. However, the validity of this assumption has not been tested. Gustavsson et al. examined the dynamic Stokes shifts of three amino-substituted coumarin dyes in methanol and dimethyl sulfoxide (DMSO) using time-resolved fluorescence spectra, concluding that, upon photoexcitation, hydrogen bonds type (i) and type (iii) are weakened or broken down, whereas hydrogen bond type (ii) is strengthened [13]. As all the coumarin dyes possess a carbonyl group, researchers have paid much more importance to hydrogen bond type (ii) than hydrogen bonds type (i) and type (iii).

The hydrogen bond dynamics in the excited state of C102 in aniline revealed that the reformation of hydrogen bonds between carbonyl oxygens and solvents takes place within 30 ps after the breakage of the same, which was found to be completed within 250 fs observed by Palit et al. [18]. However, that conclusion seems to contradict the laboratory calculations [19] for excited states of C102 in isolated (gas-phase) complexes. The hydrogen bond dynamics of C102 in acetonitrile–water binary mixtures using ultrafast spectroscopic techniques combined with Monte Carlo simulations. They suggest that excitation of C102 simultaneously weakens and strengthens hydrogen bonding in complexes with two in equivalently bound waters studied by Wells et al. [20], leading to a description of the hydrogen bond dynamics that can simultaneously accommodate both an increase in the hydrogen bond strength calculated in our laboratory and a disruption of hydrogen bonding. However, it should be noted that the Monte Carlo simulation is performed only on the ground state of C102; the suggestion of Wells and colleagues needs further examination. The hydrogen-bond cleavage and reformation also have been used to explain the rapid anisotropy decay of C460 and C153 in n-alcohols [21-22], which occurred on the order of picoseconds. According to the above discussions, it can be seen that, although a number of experimental and theoretical studies have been performed

to investigate the hydrogen dynamics in the excited state of coumarin dyes in solvents, hydrogen bonds type (i) and (iii) are not widely studied and detailed mechanisms are not clear enough.

The studies on rotational reorientation times of molecules in liquids have been an area of long- standing interest in physical chemistry and have been used comprehensively to reveal the intermolecular interactions [23–31]. The molecules in liquids interact with each other leading to various strong physicochemical properties of solutions. Reports in the literature explain several divergent approaches in experimental, theoretical and computational methods to endeavor this problem. Many studies are focused on employing two types of probes viz., nonpolar and polar. Stokes–Einstein–Debye (SED) hydrodynamic theory forms the basis of understanding molecular rotations in liquids [23] according to which, the rotational reorientation time of a solute molecule is directly proportional to its volume, bulk viscosity of the solvent and inversely proportional to the temperature. Here, the solvent is assumed to be a structureless continuum and the rotational motion of the solute is regarded as rotational reorientation times. The charge distribution of the solute molecule is believed to con tribute significantly to the friction it experiences in polar solvents [31–39].

While a considerable number of works have been reported on laser dyes in various fields with view, we focus here on the rotational reorientation of coumarin laser dyes in different media. The nature of rotational motion in solution has been a subject in physical chemistry because such motions directly reflects the interactions between a solute molecule and its surroundings. For this reason, studies of rotational dynamics provide a useful for exploring the nature of solvent friction and how it influences more complex dynamics, such as chemical reaction [23-24, 40-41].

The present work reports the rotational reorientation studies of structurally similar coumarin dyes viz., coumarin 6 (C6) and coumarin 7 (C7). These structures are expected to affect the rotational reorientation times due to the formation of hydrogen bonds with the solvent. Thus, the structures and structural changes in the solvent environment around the solute in the solvent are not fully understood. Therefore these studies investigate the rotational reorientation characteristics.

Materials and Methods:

The experimental studies were carried out in the temperature range from 298 to 342 ^{0}K, where in viscosity of solvents changes gradually 1.724 to 0.860 mPas for n-tridecane and 1.945 to 0.758 mPas in n-propanol solvent. The laser dyes C6 and C7 were of the

highest available purity obtained from Aldrich Chemical Co, and were used as received as shown in figure 1. The n-tridecane and n-propanol solvents were of spectroscopic grade and used directly. In these experiments, the concentration of the solutes was maintained in the range of 10^{-5}–10^{-6} M. The absorption and emission spectra of these dyes were recorded using UV–vis double beam ratio recording spectrophotometer (Hitachi, Model U-3200) and fluorescence spectrofluorometer (Hitachi,Model F-2000), respectively.

The rotational reorientation times of the probe molecules in alkane and alcohol solvents glycerol were measured using steady-state fluorescence depolarization technique described elsewhere [42]. For vertically polarized excitation, the steady state fluorescence anisotropy <r> can be expressed as [43, 44]

$$< r > = \frac{I_{11} - G\, I_{\perp}}{I_{11} + 2\, G\, I_{\perp}} \qquad (1)$$

where I_{11} and $I_{\perp}$ represent the fluorescence intensities parallel and perpendicular to the direction of polarization of the excitation light. G is an instrumental factor, which corrects for the polariza- tion bias in the detection system and is given by

$$G = \frac{I_{HV}}{I_{HH}} \qquad (2)$$

where I_{HV} is the fluorescence intensity when the excitation polarizer is kept horizontal with the emission polarizer vertical and I_{HH} is the fluorescence intensity when both the polarizers are kept horizontal. Each anisotropy was measured at least five times for temperature interval before taking the average value, which remained constant in the emission wavelength range. The rotational diffusion times (τ_r), when both anisotropy and fluorescence decay are represented by single exponentials, can be expressed as [44]

$$\tau_r = \frac{\tau_f}{\left[\left(\frac{r_0}{< r >}\right) - 1\right]} \qquad (3)$$

where r_0 is the limiting anisotropy when all the rotational motions are frozen and τ_f is the fluorescence lifetime.

The time resolved (TR) fluorescence measurements were carried out using an Edinburgh Instrument (model EI–199 U.K.) fluorescence spectrometer based on the time-correlated-single-photon-counting technique, described elsewhere [45], the samples of C6 and C7 were excited by 420 nm. The instrument works on the principle of time-correlated-single-photon-counting (TCSPC). Details of the TR fluorescence spectrometer have been described elsewhere [46]. The observed fluorescence decays were analyzed (using reconvolution procedure) either as a single exponential or biexponential function. The single-exponential and biexponential

nature of the fluorescence decays were judged by comparing the reduced chi-square χ^2 values and the distribution of the weighted residuals among the data channels. For the accepted fits the χ^2 values were close to unity and the weighted residuals were randomly distributed among the data channels [47, 48]. The fluorescence decays of the dyes were seen to fit well with a single-exponential function. The temperature of the samples was maintained by circulating water through the sample holder.

Results and Discussions:

Absorption and fluorescence emission spectra of molecules were recorded in n-tridecane and n-propanol solvents. Figure 2 shows the typical absorption and fluorescence spectra of C7 obtained in n-propanol solvent. The limiting anisotropy r_o was measured by dissolving the solutes in glycerol and measuring steady state anisotropy at low temperature and the values of r_o for C6 and C7 are 0.329 and 0.337. It gives the orientation of the absorption and emission transition dipoles with respect to each other. The axial radii of the molecules were estimated from the Corey-Pauling-Koltum scaled model, long axis was taken along the bond joining benzimidazole group with diethylamino coumarin and the axis perpendicular to it was taken as the short in-plane axis. The estimated axial radii of the probes C6 or C7 are 9.5 ×3.7×1.9 (axial radii/$Å^3$) and van der Waals volumes are 303 (C6) and 297 (C7) V/ $Å^3$ calculated using Edward's atomic increment method [49]. Both of these molecules are modeled as asymmetric ellipsoids.

The rotational reorientation times of C6 and C7 in n-tridecane and n-porpanol solvents as a function of temperature (T), which were obtained from the measured values of $r_{o,}$ τ_f and τ_r using equation (3) are presented in the table 1 and 2. Anisotropy <r> values for C6 are in the range of 0.0233 to 0.0106 and the τ_f values are in the range of 2.407 to 2.386 ns and τ_r values 163.9 to 71.2 ps in n-tridecane. For C7 the anisotropy values <r> (0.0277 to 0.0100), τ_f values (2.544 to 2.510 ns) and τ_r values (207.6 to 70.4 ps) are observed in-tridecane solvent. The measured values rotational motion times in n-propanol are 280.3 to 92.6 ps (C6) and 240.0 to 97.2 ps (C7) in the temperature range from 298 to 342 ^{0}K. The rotational reorientation times of a probe in the solvents are the way an index of molecular friction. Fluorescence decay of both the probes in the solvents were single exponential throughout the temperature range used in the study.

The present study has been carried out on C6 and C7 and solvents viscosity was varied by changing the temperature, the friction experienced by the solute molecule in a given solvent remain the same throughout the temperature range. The rotational reorientation times of these probes are more

or less the same in the solvent at a particular temperature. These probes however, are experiencing more friction in DMSO and n-octanenitrile similar viscosity over temperature [50]. Moog et al. [51] observed that C102 and C153, these probes are similar in size, shape and electronic charge distribution, one would expect nearly identical rotation times and hydrogen-bounding behavior for two solutes. Indeed the rotation times of probes rotates more slowly in alcohol solvents than alkanes.

The relation between τ_r and η/T $(\frac{\tau r}{\frac{\eta}{T}})$ (ps/mPas i.e. slope) of both molecules in these solvents gives linear least square fit. The τ_r values obtained for C6 and C7 are more or less the same within the limits of experimental error. Which gives for particular viscosity in both solvents indicating that, they are experiencing identical friction for particular viscosity in both solvents. Rotational reorientation times of the probes are smaller in n-tridecane compare to n-propanol, which indicates that the probe rotating faster in alcohol compared to alkane. According to general consensus, a polar molecule rotating in a polar solvent should experience dielectric friction and it is may not observed in nonpolar solvent. The higher dielectric friction experienced in n-propanol solvent by the C7 molecule compared to C6 is probably the reason why the observed rotational motion times of C7 are faster in alcohol at higher values of η/T. The free volume available for solute's rotation may be less in n-tridecane compared to n-propanol, which exists as hydrogen-bonded clusters and hence facilitates faster rotation of the probes in n-propanol solvent.

The measure of non-hydrodynamic to hydrodynamic behavior can be derived from the ratio of rotational reorientation times $\tau_{r\ alcohol(slope)}/\tau_{r\ alkane\ (slope)}$(ps/mPas) normalized to viscosity in alcohol and alkane. A ratio of unit means a perfect hydrodynamic behaviour. We obtained the results for C6 was 1.795 ps/mPas and for C7 was 0.923 ps/mPas, which indicates the deviation from hydrodynamic behavior in the solute molecule.

Conclusions:

Rotational reorientation times of two similar structures with almost identical volumes, C6 and C7 have been measured in alcohol and alkane solvents as a function of temperature. The experimental rotational correlation times are well represented as linear function of η/T. To conclude, the present results on C6 and C7 underscore the fact that we are far from having a complete understanding of how it is that the molecular details of solute-solvent interactions translate into friction on solute molecule. One of the goals for undertaking the present study is to find out which aspect is responsible for the observed trend. We may conclude that the faster rotation in OH

containing solvent than in non-OH containing solvent.

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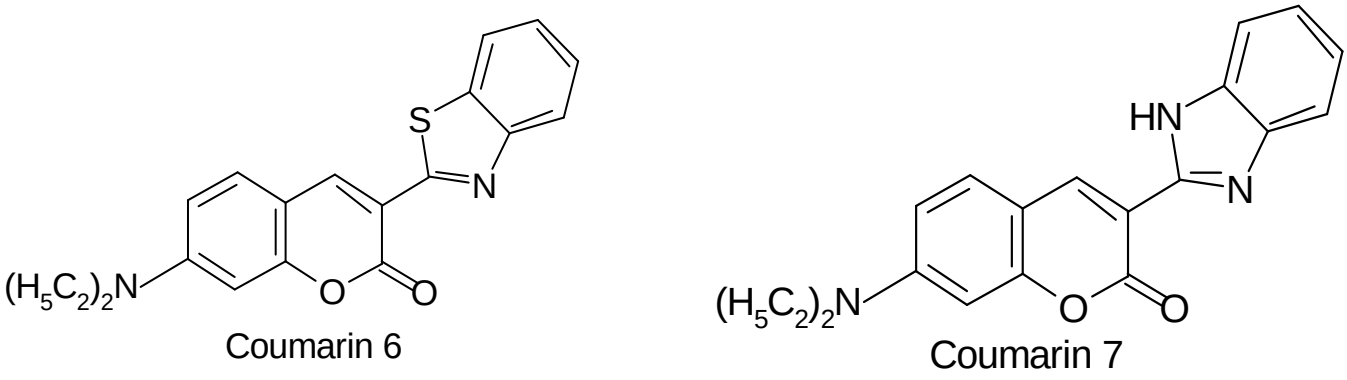

Figure 1. Molecular structures of the coumarins used in the study.

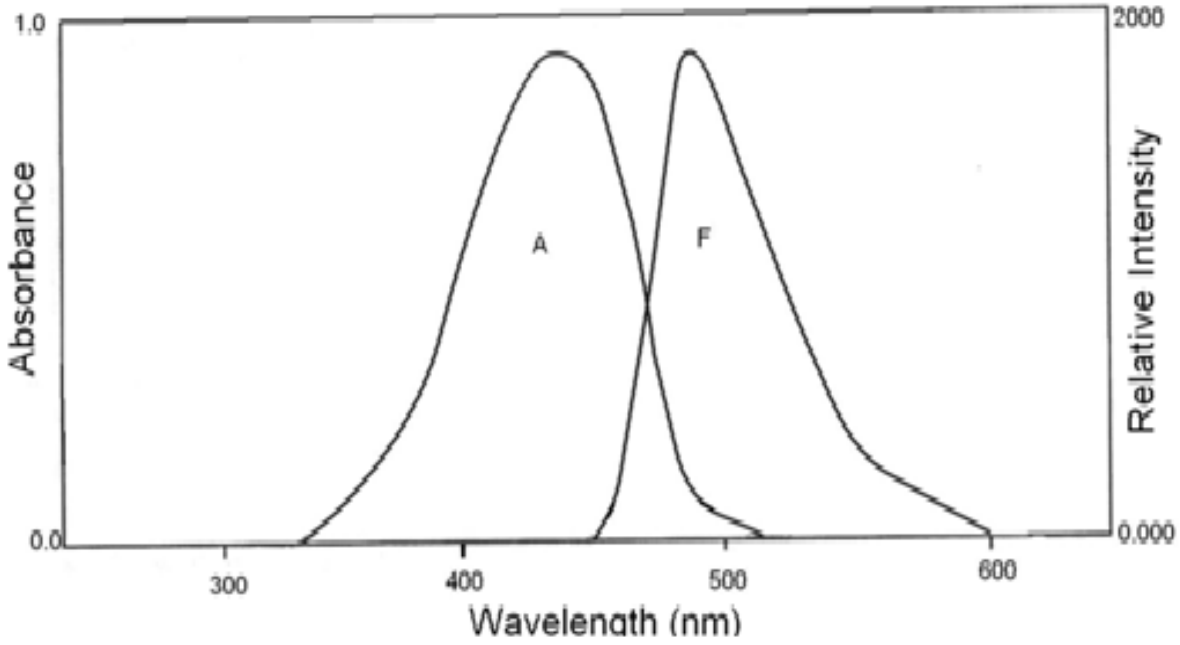

Fig. 2. Absorption (A) and Fluorescence (F) spectra of C7 in n-propanol

Table 1. Steady-state anisotropy <r>, fluorescence lifetime (τ_f) and rotational reorientation times (τ_r) of C6 and C7 in n-tridecane as function of temperature.

Temp. in ^{0}K	η/mPas	η/T *10^{-3} mPas K^{-1}	<r>	τ_f/ns	τ_r/ps	<r>	τ_f/ns	τ_r/ps
			C6			C7		
298	1.724	5.785	0.0233	2.407	163.9	0.0277	2.544	207.6
303	1.699	5.607	0.0219	2.405	146.3	0.0250	2.543	186.0
308	1.504	4.880	0.0194	2.402	134.4	0.0191	2.539	139.2
313	1.405	4.488	0.0155	2.399	106.3	0.0179	2.535	130.2
318	1.313	4.129	0.0148	2.398	101.2	0.0158	2.531	114.0
323	1.217	3.767	0.0145	2.395	99.1	0.0143	2.527	102.8
328	1.132	3.451	0.0129	2.393	87.8	0.0142	2.523	101.4
333	1.030	3.093	0.0128	2.390	87.2	0.0122	2.518	86.6
338	0.941	2.784	0.0116	2.388	75.1	0.0103	2.515	72.5
342	0.860	2.507	0.0106	2.386	71.2	0.0100	2.510	70.4

Table 2. Steady-state anisotropy <r>, fluorescence lifetime (τ_f) and rotational reorientation times (τ_r) of C6 and C7 in n-propanol as function of temperature.

Temp. in ^{0}K	η/mPas	η/T *10^{-3} mPas K^{-1}	<r>	τ_f/ns	τ_r/ps	<r>	τ_f/ns	τ_r/ps
			C6			C7		
298	1.945	6.526	0.0359	2.570	280.3	0.0301	2.696	240.0
303	1.757	5.798	0.0328	2.529	249.4	0.0282	2.690	224.4
308	1.644	5.337	0.0311	2.529	235.0	0.0267	2.695	210.8
313	1.499	4.789	0.0239	2.533	176.9	0.0241	2.710	190.0
318	1.386	4.358	0.0211	2.540	155.5	0.0238	2.712	187.6
323	1.258	3.894	0.0181	2.545	132.9	0.0192	2.710	149.2
328	1.129	3.442	0.0168	2.542	122.3	0.0170	2.711	131.3
333	1.000	3.000	0.0147	2.549	107.2	0.0152	2.715	117.0
338	0.872	2.579	0.0132	2.551	95.3	0.0132	2.716	101.0
342	0.758	2.209	0.0128	2.552	92.6	0.0127	2.719	97.2